Studies on the microwave permittivity and electromagnetic wave absorption properties of Fe-based nano-composite flakes in different sizes

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Citation: Journal of Applied Physics 118, 023902 (2015); doi: 10.1063/1.4926553
View online: http://dx.doi.org/10.1063/1.4926553
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I. INTRODUCTION

With the advancement of electronic technologies and wireless communication systems, a lot of electronic devices, such as wireless local area networks (WLAN), active radio frequency identification (RFID), and satellite broadcast systems, work normally above 1 gigahertz (GHz) in which the electromagnetic interference is a serious problem needs to be solved. It is well known that electromagnetic wave absorber is one of the most effective solutions.1–4 To further improve the absorption property, however, the traditional soft magnetic ferrites should be replaced by other materials that possess better temperature stability, higher permeability, and higher cut-off frequency.4,5 Among many candidates, Fe-based alloy flaky particle is one of the most promising electromagnetic wave absorber. However, the wide disparity between the effective permeability values and permittivity values is commonly observed for composites consisting of conducting inclusions, which can deteriorate the absorption performances.6–8

According to effective medium theory (EMT) and percolation theory, the effective permittivity ε (permeability μ) of the composite is the function of volume fraction (φ) of inclusions, dielectric constants (permeability) of inclusions, and the percolation threshold (p_c) of the composite.9–11 Near percolation, the effective permittivity of the composites can be described by an explicit law, ε = c_0 |p - p_c|^{-r}, where c_0 is the permittivity of the host matrix and ε is a critical exponent that is different for various systems.12–14 When the volume fraction of inclusions is above the percolation threshold, the electromagnetic composite behaves like a conducting medium. Around the percolation threshold, subtle variation in the volume fraction of inclusions may result in a large change in permittivity value.12–15 Therefore, it is critical to choose a suitable volume fraction of metallic inclusions in composites from the standpoint of percolation threshold. Meanwhile, the permeability spectra of both composites also have been studied by Lorentzian dispersion law. The broadened spectra can be attributed to the distribution of magnetic anisotropy fields of two kinds of ferromagnetic phases in the particles. Finally, the composite containing the small flakes exhibits better electromagnetic wave absorption properties. © 2015 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4926553]
with different sizes are investigated. Correspondingly, the electromagnetic wave absorption properties of the composites are also compared and analyzed.

II. EXPERIMENTAL DETAILS

The amorphous ribbons of Fe73.5Cu1Nb3Si13.5B9 (Fe-Cu-Nb-Si-B) were fabricated by using the well-established technique named single roller rapid solidification.18,22 Subsequent vacuum heat treatments were carried out at 540 °C for 1 h. The annealed ribbons were milled for 30 h using a planetary ball milling machine with ethyl alcohol as the milling dispersant. The weight ratio of milling balls (ZrO2) and alloys was about 25. The flake particles obtained by ball-mill technique were then sieved into two classes with different sizes. The morphologies of particles were examined by a scanning electron microscopy (SEM). The average dimensions (width and thickness) of particles were measured by the software named “Smile View.” The nanostructures of the annealed sample were investigated by a high resolution transmission electron microscopy (HR-TEM, TECNAI-G2 F20). In order to characterize the high frequency properties, the particles and wax were well mixed as composites. The composites were then moulded into the toroidal samples under a pressure of 10 MPa. The inner diameter, outer diameter, and thickness of the samples are 3.0, 7.0, and 3 mm, respectively. For each class of particles, the effective microwave permittivity and permeability of a composite sample containing 27.99% (volume fraction) particles were measured based on the so-called Nicolson-Ross-Weir principle24 on a Vector Network Analyzer (Agilent 8720ET) within a frequency range of 0.5–10 GHz at room temperature.24 As for smaller particles (see Fig. 1(c)), the range of width of particles is 1–23 μm with the average width and thickness about 8.1 μm and 1.0 μm, respectively.

The measured microwave effective permittivity values of the composites are presented in Fig. 2. For the large flake composite, the real part (ε′) and imaginary part (ε″) of the effective permittivity at the starting measuring point (0.5 GHz) are about 75.4 and 64.8, respectively. Both ε′ and ε″ quickly decrease with frequency and show large dielectric losses within the measuring frequency range. For the small flake composite, ε′ and ε″ are about 32.9 and 2.7, respectively. Both ε′ and ε″ change slowly and an obvious dielectric relaxation peak is observed in the frequency range of 0.5–3 GHz. However, no peaks associated with the dielectric loss could be found for the large flakes. It is noteworthy that both real and imaginary parts of effective permittivity for large flake composite are much higher than those of small one.

According to the harmonic oscillator model, the dynamic response of permittivity and permeability generally behave like relaxation type or resonance type. Debye model and Cole-Cole model, as well as their deformations correspond to the relaxation type. Lorentz model and its deformations characterize the resonance type. When the Lorentzian damping constant is as large as 10, the resonance behavior completely transforms into the ideal relaxation behavior.26–29 The peak in the permittivity spectra indicates the existence of the polarization relaxation.30 Generally, there exist interfacial polarization and dipolar polarization at microwave frequencies.30,31 However, there are no permanent dipoles in our alloy-paraffin composite system. Hence, the dielectric relaxation could be attributed to the interfacial relaxation originating from the polarization at the flakes-paraffin interfaces.

The Cole-Cole plot is an effective approach to check whether or not the selected model is applicable. For the relaxation type, only the Debye model and Cole-Cole model behave like symmetrical Cole-Cole plots.30,32 In our case, the Cole-Cole plots which are depicted for the composites containing both classes of flakes are shown in Fig. 3. The distorted Cole-Cole semicircles are found for both composites, especially for the composite containing large flakes. Therefore, the asymmetric Cole-Davidson model is chosen in the analysis. Similarly, the Lorentz model with damping, which characterizes a distorted Cole-Cole semicircle, is used as well. These choices had been experimentally evidenced by Ref. 26. It should be stressed that the large deviations of the Cole-Cole semicircles are found for both composites near the starting measurement frequency. According to
Refs. 33–37, those large deviations could be attributed to the conductivity which are caused by the diffusion of charge carriers in alloy composites under the external microwave fields. Therefore, the Cole-Davidson law and Lorentzian law have been modified in this paper to take into account of the contribution of conductivity.

Equations (1) and (2) were corresponding to the revised Cole-Davidson law and Lorentzian law, respectively,

\[
\varepsilon = \varepsilon_{\infty} + \frac{\varepsilon_0 - \varepsilon_{\infty}}{(1 + j\omega\tau)^2} - \frac{\sigma}{\varepsilon_0\omega} \quad (0 < \beta \leq 1, 0 < t \leq 1), \quad (1)
\]

\[
\varepsilon = \varepsilon_{\infty} + \frac{\varepsilon_0 - \varepsilon_{\infty}}{1 - (f/f_r)^2} - \frac{\sigma}{\varepsilon_0\omega} \quad (0 < t \leq 1), \quad (2)
\]

where \(\varepsilon_0\) is the permittivity of free space \(\varepsilon_0 = 8.85 \times 10^{-12} F/m\) and \(\varepsilon_0\) and \(\varepsilon_{\infty}\) are dielectric constant of composite at \(f=0\) and \(f=\infty\), \(\tau = (2\pi f_0)^{-1}\) is the relaxation time for the interface polarization processes and \(f_r\) is the relaxation or resonance frequency. \(\omega\) is the angular frequency. \(\beta\) \((0 < \beta \leq 1)\) is the asymmetric factor. \(\gamma\) is the damping factor of Lorentzian law. \(\tau\) is an exponent \((0 < t \leq 1)\), which indicates the ohmic behavior.\(^{37,56}\) The closer the \(\tau\) value approaches unit, the more ideal the ohmic behavior is. At low frequency, the parameter \(\sigma\) can be replaced by the \(dc\) conductivity \((\sigma dc)\). When the discussions fall in the microwave scope, \(\sigma\) should be in a complex number, which can be expressed as \(\sigma = \sigma_1 + j\sigma_2\), where \(\sigma_1 = \sigma_1' + j\sigma_2'\) and \(\sigma_2 = \sigma_2' + j\sigma_2''\).\(^{34,35,39}\) The \(ac\) conductivity \((\sigma ac)\) can be expressed as the real part of \(\sigma\). Due to the \(\omega\), it is in large magnitude, \(\sigma ac\) values are mainly determined by the \(\sigma_2''\) values.

As shown in Fig. 3, the fitting curves of modified Lorentzian law agree better with the experimental data than the modified Cole-Davidson law does. The fitted values are given in Table I. As listed in Table I, the damping constant \((\gamma\) in Lorentzian law for large flakes is about 4.16, while it is about 2.96 for the small ones. These large damping constants denote that the frequency dependence of effective permittivity should belong to the relaxation type rather than the resonance type. The asymmetric factors \(\beta\) in Cole-Davidson law for large and small flakes are 0.63 and 1.00, respectively. Due to the unit value of \(\beta\), the Cole-Davidson model for the small flakes degenerates to the symmetric Debye model, which also can be deduced from the symmetric loss peak and Cole-Cole plot, as shown in Figs. 2(b) and 3(b). \(\varepsilon''\) and \(\sigma_2''\) values of large flakes are much larger than those of small flakes, which implies that the conducting network established by the large flakes has more notable influence for the effective microwave permittivity. The fitted value of \(\tau\) is close to 1, indicating the existence of ohmic contact between the large flakes in the composite. Nevertheless, as for the composite consisting of small flakes, the value of \(\tau\) is found to be about 0.5. Hence, we could conclude that the ohmic contacts between larger flakes lead to the formation of a conducting network, which induce the enhancement of the high-frequency effective permittivity.

The percolation threshold \((p_c)\) can be obtained based on the Odelevsky law,\(^{2,40}\) \(\varepsilon(p_c)/\varepsilon_b = 1 + p/(N(1-p/c))\), where \(\varepsilon\) is the effective permittivity of the composite and \(N\) is the demagnetization factor in the direction of width for the flakes. First, the frequency dependences of permittivity for composites with different volume fractions \((0, 4.93\%, 11.47\%, 20.58\%, \text{and} 27.99\%)\) of flakes have been measured (not shown here). Second, the normalized permittivity values of composites have been fitted employing the above equation. The \(p_c\) values for the composites containing the large and small flakes are found to be 34.8% and 37.6%, respectively. Both \(p_c\) values are higher than the volume fraction \((27.99\%)\) of composites discussed in this paper. Such \(p_c\) values are much higher than other slender metal inclusions. This result can be attributed to lower conductivity caused by the unique nanostructure and smaller aspect ratios of our

FIG. 2. Microwave permittivity of composites containing flakes: (a) large flakes and (b) small flakes. The open symbols represent the experimental data.

FIG. 3. Cole-Cole plots of the permittivity values for both composites: (a) large flakes and (b) small flakes.
alloy particles when comparing with other slender metal inclusions. The composite with large flakes has a smaller $p_c$ value than that of composite with small ones, which also justify the previous conclusion that the conducting mechanism among the flakes more commonly prevails within the composite containing the large flakes.

According to our previous work, the eddy current effect is significant above 1.3 GHz in composites consisting of large flakes, while it can be neglected in the composite consisting of small flakes within the measurement frequency range.\(^3\) In other words, skin depth is larger than the average thickness of small flakes. Although the observed effective microwave permittivity values are large for the large flakes, they are not as large as they should be. It is because that only part of materials reacts with the electromagnetic wave due to the fact that the skin depth in large flakes is smaller than the average thickness of flakes.\(^16\) On the other hand, the eddy current effect, which drives the charge carriers onto the surface of particles in the skin depth, leads to the eddy current density redistribution. The eddy current density on the surface of large flakes is much larger than that of small ones, as indicated by the relationship: \(^41\) 

\[
\rho \frac{d^2J_{eddy}(y)}{dy^2} = \frac{2\pi y B_m}{\rho}, \quad \text{where} \quad B_m \quad \text{is the magnitude of magnetic current.} \]

\[
\rho \quad \text{is the resistivity value.} \]

The quantity of interfacial charges in the large flaky composite is much larger than the small ones due to the larger $y$ values. In addition, from our SEM data, the average aspect ratio of large flakes is much larger than that of small ones. According to Ref. 42, the quantity of interfacial charges in the composites is also determined by the aspect ratio of inclusions rather than the size of inclusions. Consequently, the quantity of interfacial charges in the composite with large flakes can be larger than those in composite with small flakes, which is a decisive factor in determining the high-frequency effective permittivity values. As a result, the larger effective permittivity can be obtained in large flakes. Although large dielectric losses associated with the composite containing large flakes show that the energy of incident electromagnetic wave could be dissipated, the impedance mismatch becomes more serious, which hampers the improvement of the absorption properties.

In order to investigate the high frequency behaviors of electron transport in conducting inclusions by studying the dielectric spectra, the $\text{ac}$ conductivity of our samples have been calculated from the dielectric losses according to the following equation: \(^35\)

\[
\sigma = j\mu_0\omega\epsilon = j\mu_0\omega(\epsilon' - j\epsilon'') = \epsilon_0\omega\epsilon'' + j\mu_0\omega\epsilon',
\]

the $\text{ac}$ conductivity is given as

\[
\sigma_{ac} = \text{Re} [\sigma] = \epsilon_0\omega\epsilon''.
\]

The plots of $\sigma_{ac}$ versus $f$ are shown in Fig. 4. The $\text{ac}$ conductivity becomes larger with increasing frequency. The spread-out peaks for large and small flakes locate at $f = 1.91$ GHz and at $f = 3.98$ GHz, which are in accordance with the previous dielectric spectra. The $\text{ac}$ conductivities of large flakes are larger than those of small flakes in the whole measurement frequency range. Such an obvious difference in conductivities also can be inferred from the previous percolation values of composites. Generally speaking, the frequency dependence of conductivity can be understood as follows. At low frequency, the charge carriers can be drifted over large distances under the applied $\text{ac}$ electric field. Moreover, there are sufficient numbers of quasi-free, slowly mobile carriers, which retain the conductivity almost as $dc$ conductivity values. As the frequency increases, the mean migration distance of charge carriers will be reduced. Once reaching a critical frequency ($f_c$), the values of conductivity increase rapidly and obey the law: $\sigma_{ac}(\omega) \sim \omega^\mu (0 \leq \mu \leq 1)$, which describes the frequency dependence of conductivity for materials with a good semiconducting feature. \(^35,43,44\)

To investigate the charge transport at high frequency in the alloy flakes-paraffin composite, the hopping mechanism of charge carriers named “the $\text{ac}$ universality law” is employed to fit the $\text{ac}$ conductivity spectra. At room temperature, it can be expressed as \(^43,45\)

\[
\sigma_{ac}(\omega) \sim \omega^\mu.
\]

| Table I. The fitted values of parameters appeared in Eqs. (1) and (2). |
|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| Types of laws | $\epsilon_s$ | $\epsilon_{\infty}$ | $f_c$ (GHz) | $\beta$ or $\gamma$ | $\tau$ | $\sigma_1'$ (S/m) | $\sigma_1''$ (S/m) | $\sigma_2'$ (S/m) | $\sigma_2''$ (S/m) |
| Large flakes | Cole-Davidson | 96.50 | 52.16 | 0.72 | 0.63 (p) | 0.95 | $1.12 \times 10^{-10}$ | $7.45 \times 10^{-11}$ | $-2.24 \times 10^{-10}$ | $-2.77 \times 10^{-9}$ |
| Lorentzian | 402.14 | 382.14 | 2.05 | 4.16 (q) | 0.97 | $9.50 \times 10^{-10}$ | $4.74 \times 10^{-11}$ | $1.47 \times 10^{-10}$ | $-2.77 \times 10^{-9}$ |
| Small flakes | Cole-Davidson | 39.00 | 29.00 | 4.12 | 1.00 (p) | 1.00 | $-3.33 \times 10^{-11}$ | $5.54 \times 10^{-12}$ | $1.30 \times 10^{-11}$ | $-5.39 \times 10^{-11}$ |
| Lorentzian | 34.12 | 31.51 | 4.01 | 2.96 (q) | 0.50 | $1.63 \times 10^{-11}$ | $8.22 \times 10^{-13}$ | $6.04 \times 10^{-12}$ | $-7.01 \times 10^{-12}$ |

Fig. 4. The $\text{ac}$ conductivity ($\sigma_{ac}$) versus $f$ of the composites with (a) large flakes and (b) small flakes.
In the case of the composite with large flakes, $\mu_{max}$ is about 2.1, while it is about 1.6 for the composite with small flakes.

In our previous work,7 the differences in the effective microwave permeability have already been studied. It was believed that the natural resonance of spins rotation and the eddy current effect are critical factors affecting the observed differences. Our assumption about the origins of wide magnetic loss peaks is that the distributions of particle sizes and grains sizes and the random orientation of particles in composites will result in the distribution of magnetic anisotropy fields, which will give rise to the distribution of natural resonances of spins rotation.46 The Lorentzian dispersion law is frequently used to describe the frequency dependence of permeability.47 Since there are two magnetic phases in our Fe-based nanocomposite flakes, an equation consisted of two Lorentzian components is proposed to fit the measured spectra in this study, as given below

$$\mu(f) = 1 + \sum_{i=1}^{2} \frac{\mu_{si} - 1}{1 + j\beta_i (f/f_{ri}) - (f/f_{ri})^2},$$

where “$\mu_{si}$” is the static permeability, “$f_{ri}$” is the resonant frequency, “$\beta_i$” is the Lorentzian damping parameter (not the Gilbert’s damping parameter), and “$f$” is frequency. As shown in Fig. 5, the fittings agree well with experimental data. The fitted values are listed in Table III.

When the composite containing the flakes is used as a singler layer electromagnetic wave absorber on a perfect conducting plate, the absorption properties of normal incident electromagnetic wave can be expressed in terms of reflection loss ($RL$). The $RL$ values can be calculated based on the following equations:

$$Z_{in} = Z_0 \sqrt{\frac{\mu}{\varepsilon}} \tanh \left( \frac{2\pi f d}{c} \sqrt{\mu \varepsilon} \right),$$

$$RL = 20 \log \left| \frac{Z_{in} - Z_0}{Z_{in} + Z_0} \right|,$$

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where $Z_0 = \sqrt{\mu_0/\varepsilon_0}$ is the intrinsic impedance of free space, $c$ is the speed of light, $d$ is the thickness of the absorber, and $\varepsilon$ and $\mu$ are the relative complex permittivity and permeability of the absorber, respectively. The contour maps are drawn to show the potential absorption performances of composites with different thickness, as shown in Fig. 6. For the composite containing small flakes, the absorption bandwidth is larger than 1 GHz if the thickness of composite falls into the range of 2–4 mm. Clearly, the composite with small flakes can exhibit much better microwave absorbing properties, which will enable the Fe-based nanocomposite flakes to find potential applications in electromagnetic wave attenuation with operation frequency above 1 GHz.

To better understand the reflection losses of composites from the perspective of impedance matching, the relationship between the absorber thickness and the matching frequency is expressed as follows: $d_m = \frac{2}{\lambda} = \frac{1}{2\pi \nu} \left( \text{Re} \left[ \sqrt{\varepsilon \mu} \right] \right)^{-1}$, where $\lambda$ is the wavelength, $\tan \delta_c$ and $\tan \delta_m$ are the loss tangents of permittivity and permeability, $f_m$ is the matching frequency, and $d_m$ is the absorber thickness when the impedance is matched. According to this equation, both the magnetic loss and dielectric loss make contributions to the dissipation of incident electromagnetic energy. In addition, “$f_m$” is inverse to “$d_m$”, which means that the matching frequency (i.e., the $RL$ values reach a minimum value) moves toward the lower frequency with increasing the thickness of absorber, as shown in Fig. 7(a). In our case, the values of $\text{Re} \left[ \sqrt{\varepsilon \mu} \right]$ for composite with large flakes are larger than those of composite with small flakes. At a given thickness (for instance, 4 mm), the matching frequency ($f_m$) of composite containing large flakes is smaller, see Fig. 7(b). Clearly, the absorber with smaller flakes as the magnetic inclusions exhibits better electromagnetic wave attenuation performances.

IV. SUMMARY

Fe-based micro flakes with nanocomposite nanostructures have been manufactured. The obvious differences in microwave permittivity of composites containing flakes in different sizes have been observed. The results show that the larger flakes have larger values in both real parts and imaginary parts of permittivity. It is believed that the interfacial polarization and eddy current effect are critical factors affecting the observed differences in microwave permittivity. Furthermore, for the composites containing large flakes, the ohmic contacts among flakes are found to be more extensive, indicating the character of semiconducting materials. While the composites containing the smaller flakes show the character of insulating materials. Finally, the composites containing the smaller flakes show better electromagnetic wave absorption properties.

ACKNOWLEDGMENTS

This work was funded by the National Natural Science Foundation of China (Grant No. 61271039) and the Scientific Foundation of Outstanding Young Scientists in Sichuan Province (Grant Nos. 2012JQ0053 and 2013JQ0006). It was also supported by the Open Foundation of National Engineering Research Center of Electromagnetic Radiation Control Materials (ZYGX2014K003-4).
